Absence of Quantum Criticality and Bulk 3D Magnetism in Green Dioptase

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Abstract –Green dioptase is a naturally occurring antiferromagnetic mineral that in recent years has been suggested as a candidate to exhibit quantum fluctuations at both above and below T_{N}. Our work uses muon spectroscopy to study the dynamic and static properties of the magnetism in zero-applied field. We observe the antiferromagnetic transition through tracking out the evolution of the muon precession frequency as a function of temperature. T_{N} is calculated to be 15 K and the critical order parameter of the transition matches with that of a 3D Heisenberg system. We also note that no evidence for any quantum magnetic fluctuations are observed either above or below T_{N}.

Introduction. – Gemstones have fascinated people and societies for centuries, where they have garnished and adorned various precious items such as jewellery. The natural origin of gemstones has also presented scientists with the challenge of understanding them and essentially studying nature's playground. Green Dioptase is one such precious mineral that forms dark green crystals with the empirical formula $CuSiO_3{\cdot}H_2O$ and has found favour within the crystal healing community. Green dioptase crystallises with $R\bar{3}$ symmetry with Si_6O_{18} rings intersected by Cu^{2+} ions. The Cu ions form quasi 1D helical chains that run along the *c*-direction within the crystalline axes (see Figure 1). Each Cu ion has two intra-chain nearest neighbours and an additional Cu ion on the adjacent chain [1,2], thus each Cu ion only has three other Cu nearest neighbours. The water molecules sit in positions between the silicate rings where one proton of each water forms a bent O-H bond with an O on the silicate ring as elucidated by NMR measurements [3].

The magnetic properties of green dioptase have been a point of recent discussion. It was first measured by Wintenberger *et al.* [4] where a broad hump was seen with a maximum at 50 K and an approximate fit to Curie-Weiss law suggested that the sample was antiferromagnetic in

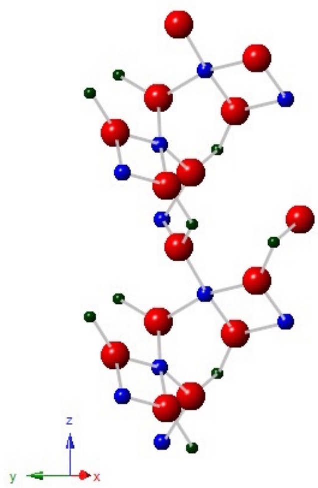

Fig. 1: Crystal structure of green dioptase selectively cut to illustrate the nature of the quasi-1D Cu-O chains along the *c* or *z*-direction of the unit cell. Note that Cu ions are blue, O ions are red and Si ions are green in the image.

nature. From neutron diffraction data, the antiferromagnetic structure could be solved confirming the nature of the low temperature magnetism [2]. ESR measurements showed a shift in the resonance frequency at 50 K where there was a maximum in the magnetic susceptibility, but there was the clear onset of an antiferromagnetic ground state with an energy gap of 350 GHz ($\sim$ 17 K) [5]. Recent reports have, however, suggested that green dioptase is an ideal candidate to show quantum critical behaviour since the inter- and intra- chain exchange energies may be similar leading to frustration and a dynamic magnetic ground state [6]. Further work was conducted that suggested that strong quantum fluctuations were present in the broad maximum in the magnetic susceptibility but theoretical models suggested that the system is 3D and not frustrated [7]. Very recently, inelastic neutron scattering measurements at temperatures well below T_{N} showed that the magnetic structure is a spiralled AFM along the spin chains [8] but there was no evidence for any quantum fluctuations.

There is still some ambiguity in the magnetic behaviour of green dioptase where additional techniques are required. To this end we employ muon spectroscopy (μSR) to help study any potential magnetic quantum fluctuations or static order in zero-applied field. μSR is a technique that is sensitive to both dynamic and static magnetic behaviour. In the past, μSR has proved useful for showing that at low temperatures magnetic systems have strong dynamic character from frustration and quantum critical fluctuations [9–12]. Using μSR, we have been able to show that green dioptase orders at approximately 15 K where there is no evidence of magnetic fluctuations below T_{N}. Above T_{N}, the muon spin relaxation measurements show the muon couples only to nuclear moments, however there is also no evidence of electronic fluctuations.

Experimental. – The green dioptase crystals were purchased from Crystal Classics [13] sourced from Namibia. Crystals of green dioptase were then ground up to be used within measurements where X-Ray diffraction and X-Ray fluorescence spectroscopy was used to confirm all samples were phase pure.

Magnetic susceptibility measurements were performed on a Quantum Design SQUID VSM with fields capable of up to 7 T. Muon spin relaxation/rotation (μSR) measurements were conducted on the EMU instrument at the ISIS Neutron and Muon Source. The μSR technique involves implanting a spin polarised ensemble of positive muons in the sample and monitoring the time evolution of the the muon spin polarisation through the asymmetry in the forward and backward directions of the positron decay that occurs with a half-life of 2.2 μs. Thus the technique is sensitive to processes on the MHz time scale. The muon is a local probe, sampling a radius of approximately 2 nm and upon implantation in the sample is sensitive to both local nuclear and electronic moments. If the local, internal magnetic field is homogeneous at the muon site, the muon ensemble will precess coherently and this precession frequency, $\nu = \gamma_\mu \cdot B_{\mathrm{int}}$ where γ_μ is the gyromagnetic ratio of the muon and B_{int} is the internal magnetic field at the muon site. If however, the internal field experienced by the muon becomes more inhomogeneous, then the field distribution increases and this leads to a dephasing of the muon ensembles spin and one sees a damping or relaxation of the precession signal.

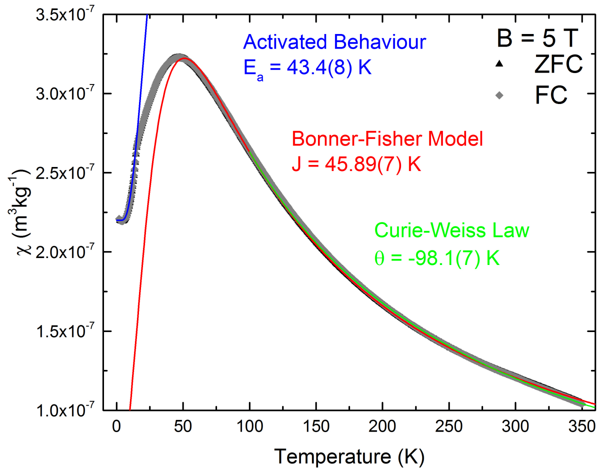

Fig. 2: Temperature dependence of the ZFC and FC magnetic susceptibility where the data were taken in an applied field of 5 T. The solid lines are fits to the data.

Results and Discussion. – Magnetic susceptibility measurements have previously been reported for green dioptase [4, 7]. Our data shows similar behaviour where there is a gradual increase in the susceptibility with a maximum at approximately 50 K. There is then a decrease and an obvious change in slope occurs below 25 K, which is likely to be the emergence of the magnetically ordered phase. This type of behaviour has been seen within other 1D systems [14]. A fit to the high temperature data to Curie-Weiss law showed good agreement, however the value of $\theta = -98.1(7)$ K, suggesting an antiferromagnetic (AF) ground state. The frustration parameter, $f = -\theta/T_{\mathrm{N}}$ is calculated to be 6.6, which shows there is a fairly strong suppression of order. Given the 1D nature of the sample and the $S = 1/2$ moments on the Cu ions, a better approximation may be the Bonner-Fisher model [15], which is a mathematical expansion that describes increasing interactions along an antiferromagnetically coupled 1D $S = 1/2$ chain. The value of J, the exchange energy extracted from this fit is 45.89(7) K, where there is good agreement between the fit and temperatures above 75 K. However, as the temperature reaches 50 K and the susceptibility goes through the maximum, the fit breaks down and cannot fit the broad peak. At 50 K, there may be increasing inter-chain interactions that lead to to a break down in the 1D behaviour of the sample. Since the sample has been reported to be in an AF ground state at the lowest temperatures, this would be accompanied by the opening of a spin gap and so it seems sensible to model the low temperature susceptibility with an activated behaviour such as;

$$\chi = A\exp(-E_{\mathrm{a}}/k_{\mathrm{B}}T) \qquad (1)$$

where A is the pre-exponent and E_{a} is the activation or spin gap energy and thus a measure of J. From the fits the estimate of the spin gap is 43.4(8) K. This is an indication of the exchange energy associated with the ordered phase and this is close to the intra-chain exchange energy calculated from the fits to the Bonner-Fisher model. This could also be an indication that the inter- and intra-chain interactions are very close in value and this may put the system on the edge of a 1D to 3D behaviour.

In order to further study the nature of this low temperature ($T < 50$ K) transition μSR was used. This presents a unique zero-field (ZF) probe and has advantages for studying critical behaviour of materials. The raw data can be seen in Figure 3. The high temperature data were taken between 30 and 50 K where there was no apparent difference between the muon spectra. This allowed for a high temperature spectra with high statistics to be collected and analysed. The raw data resemble that observed by Cottrell *et al.* [16] who attributed such a low frequency oscillation in the baseline to the muon binding to a deprotonated oxygen and with some anisotropy in the position of the nuclear moments relative to the muon site. In our case, the high temperature data could be fitted using a summation of 2 components; the first is a theory developed by Meier [17] that accounts for the muon spin relaxation from dipolar interactions with surrounding nuclei with an exponential damping and the second is an additional Gaussian relaxation. This implies that there are two muon stopping positions within the sample and with a ratio of 0.66:0.34 between component 1 and 2 respectively, the baseline is low at 1.32%. The strong anisotropic homogeneous dipolar coupling from the first component produces oscillations in the tail of the relaxation with a field at the muon site of 7.46(2) G and a damping of 0.094(2) MHz. As for the second Gaussian component, this has a damping of 0.162(3) MHz, and so the broader field distribution represents a site with more field inhomogeneity. More work will be conducted on the high temperature behaviour of the sample and reported elsewhere [18], however, there is no evidence that there are any electronic fluctuations above T_{N}.

For the low temperature ($T < 30$ K) data high statistics spectra were collected in order to resolve the heavily damped oscillation at short times, as can be seen in Figure 3 and indicates the presence of magnetic order in the sample. On first glance, it is clear that there is a large drop in initial asymmetry that is congruent within the onset of a bulk magnetically ordered state. This drop in the asymmetry is due to large internal fields causing many of the muons to dephase outside of the experimental time scale. Although at high temperatures there appears to be two

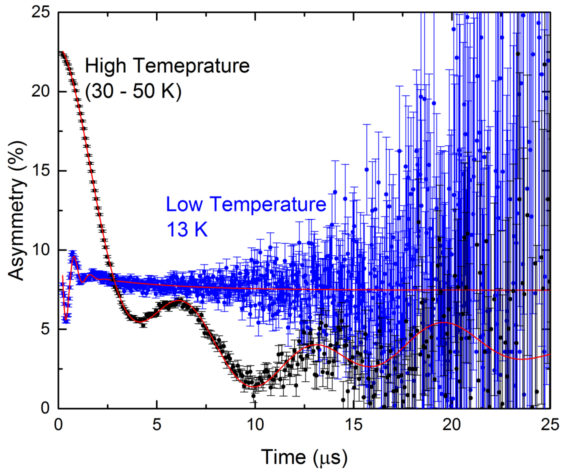

Fig. 3: Raw data from the muon spectroscopy experiments. The high temperature data were co-added between 30 and 50 K to present a high statistics spectra to fit to since there was no apparent change in the relaxation with temperature. The low temperature data is shown at 13 K where the sample is within the critical region.

muon sites, this is harder to detect in the lower temperature data and it is therefore likely that the two sites have very similar frequencies or one has a frequency outside our time window making them hard to resolve, especially given that the raw data have high statistics. Therefore, in order to parametrise and gain a value for the critical parameter a reasonable fit was achieved using a single oscillatory component:

$$G(t) = A_1(\cos(\omega t)\exp(-\lambda_1 t)) + A_2\exp(-\lambda_2 t) + A_{\mathrm{B}} \quad (2)$$

where A_{n} is the asymmetry of the relative components, ω is the frequency of the muon spin precession that is related to the internal field at the muon site by $\omega = \gamma_\mu B$, λ_{n} is the relaxation that describes the field distribution and A_{B} is the baseline. In the ordered phase, the baseline is around 7.4% and the asymmetries are fairly constant as is the value for λ_2 at 0.32 MHz. λ_1 shows a gradual increase with decreasing temperature, which can be seen in the supplementary information. Below 9 K, the damping appears, within error, to be constant. The gradual rise in λ_1 is likely due to the increasing field broadening due to the highly anisotropic 1D system; as the electronic moments order, these will be along the 1D chains and the muon will be in a position of an inhomogeneous field distribution.

The temperature dependence of the muon spin rotational frequency from fits to Equation 2 can be seen in Figure 4. The frequency *vs.* temperature data could be fit within the critical region with the equation

$$\omega = D(1 - T/T_{\mathrm{C}})^{\beta} \qquad (3)$$

where D is the frequency at 0 K and β is the critical exponent. From the fits solely in the critical region, $\beta = 0.37(1)$, which is similar to what is expected for a

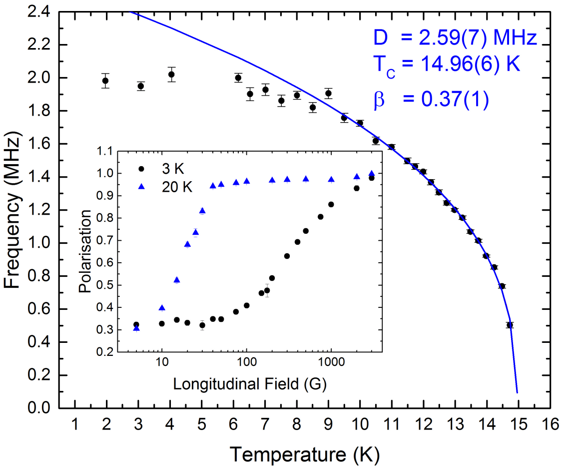

Fig. 4: The frequency of the muon precession as a function of temperature. The solid line is a fit to the data using Equation 3 to get the critical exponent and corresponding T_{C}. *Inset:* The longitudinal field dependence of the muon polarisation associated with the baseline observed at temperatures above and below the T_{C}.

3D Heisenberg bulk system. The value of T_{C} equates to 14.96(6) K, and this is approximately where we observe the kink in the magnetic susceptibility at low temperatures. Therefore at this point the system falls into a 3D ordered ground state.

To further confirm this, a longitudinal field (LF) sweep was conducted, where the application of an LF decouples the polarisation of the muon spin from the surrounding environment, thus at higher fields you will always recover to a polarisation of 1. The data can be seen in the inset of Figure 4, where there is a clear difference between the low and high temperature LF sweeps. At 20 K, the muon polarisation is fully recovered at 40 G, which is typical of a muon - nuclear moment dipole interaction. There is no indication of dynamics of nuclear or electronic moments on the muon time scale otherwise; it would require a larger field to decouple the muon spin. At low temperatures, much larger fields are needed to begin decouple the muon spin from the internal fields, there may be a change of slope at 300 G, with the mid-point of the curve at ~150 G (2.03 MHz). There is then a slow increase in the polarisation, which might suggest that the second muon stopping site sits in a region where the internal fields are too high for us to measure with the experimental technique. It should be noted that at the higher fields (> 1 kG) there is no relaxation and the spectra are essentially a flat line; therefore there is no evidence of electronic fluctuations on the muon time scale.

If there was observation of quantum critical behaviour, then the electronic moments would be dynamic and the muon spin relaxation measurements would reflect this. Evidence, for example, would be no dramatic loss in asymmetry on going through T_{N}; one would simply expect either there to be no apparent relaxation since the muon would be in the motionally narrowed state, or a relaxation but no missing asymmetry, provided the fluctuations were within the experimental time window. One would also expect to see a relaxation even in applied fields, where, once the nuclear moments had been decoupled, the electronic fluctuations would not be perturbed by the applied field and so the muon will not be decoupled from the dynamics. Instead we observe no evidence of any strong relaxation that would suggest the sample is in a dynamic state colorredwithin the experimental time-scale. The muon spectra resemble that of a system that has magnetically ordered where the baseline has shifted higher in asymmetry to approximately 1/3, which is expected when in the ordered state, where one has a $x/3 + y/3 + z/3$ average; a purely dynamic state would not be accompanied by this missing asymmetry. The onset of the oscillatory component is a clear indication of a bulk ordered phase, albeit with a significant damping. The calculated critical exponent associated with the transition matches well with that expected for a 3D Heisenberg magnet and given previous work [2, 8], it is certainly antiferromagnetic in nature.

Concluding Remarks. – In summary, we have studied the nature of the antiferromagnetic transition in green dioptase using magnetic susceptibility and muon spectroscopy.The order parameter associated with the transition, obtained from the temperature dependence of the muon spin rotational frequency, showed the sample orders to a 3D Heisenberg ground state. We find that there is no evidence of quantum critical behaviour above or below T_{N}. Instead, below T_{N} the sample appears to enter a static state magnetic state on the time scale of the muon measurement.

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REFERENCES

[1] H. G. Heide and K. Boll-Dornberger. *Acta Crystallogr.* **8** (1955) 425
[2] E. L. Belokoneva, Yu. K. Gubina, J. B. Forsyth and P. J. Brown. *Phys. chem. Minerals.* **29** (2002) 430
[3] R. D. Spence and J. H. Muller. *J. Chem. Phys.* **29** (1958) 961
[4] M. Wintenberger, G. André and M. R. Gardette. *Sol. Stat. Commun.* **87** (1993) 309
[5] H. Ohta, S. Okubo, N. Souda, M. Tommo, T. Sakurai, T. Yoshida, E. Ohmichi, M. Fujisawa, H. Tanaka and R. Kato. *App. Mag. Reson.* **35** (2009) 35
[6] C. Gros, P. Lemmens, K.-Y. Choi, G. Guntherodt, M. Baenitz and H. H. Otto. *EuroPhys. Letts.* **60** (2002) 276

[7] O. Janson, A. A. Tsirlin, M. Schmitt and H. Rosner. *Phys. Rev. B.* **82** (2010) 014424
[8] A. Podlesnyak, L. M. Anovitz, A. I. Kolesnikov, M. Matsuda, T. R. Prisk, S. Toth and G. Ehlers. *Phys. Rev. B.* **93** (2016) 064426
[9] T. Suzuki, F. Yamada, T. Kawamata, I. Watanabe, T. Goto and H. Tanaka. *Phys. Rev. B* **79** (2009) 104409
[10] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato and G. Saito. *Phys. Rev. Letts.* **91** (2003) 107001
[11] T. Itou, A. Oyamada, S. Maegawa, M. Tamura and R. Kato. *J. Phys.: Condens. Matter.* **19** (2007) 145247
[12] P. Mendels, F. Bert, M. A. de Vries, A. Olariu, A. Harrison, F. Duc, J. C. Trombe, J. S. Lord, A. Amato, and C. Baines. *Phys. Rev. Letts.* **98** (2007) 077204
[13] https://www.crystalclassics.co.uk/
[14] *Extended Linear Chain Compounds: Volume 3* Ed. J. S. Miller (1983) Plenum Press, New York.
[15] J. Bonner and M. Fisher. *Phys. Rev.* **135** (1964) A640
[16] S. P. Cottrell, J. S. Lord and W. G. Williams. *J. Phys. Chem. Solids* **62** (2001) 1977
[17] P. F. Meier. *Hyperfine Interact.* **17-19** (1984) 427
[18] *In preparation.*